Novel Scalable Synthesis of Luminescent and Magnetic Single Crystal Garnets

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Supporting Information

Experimental procedure:

Synthesis of glasses and crystals: The raw materials used in the synthesis (GeO_2, Bi_2O_3, Ga_2O_3, PbO, Al_2O_3, Fe_2O_3, and RE_2O_3 (with RE = Ce^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Y^{3+}, Sc^{3+})) were 99,99% purity grade. Typical synthesis batches of 5 g containing the desired composition were homogenized using a speed-mixer equipment for 5 min, before it be transferred to a platinum crucible (cup format) and be placed into a pre-heated furnace at 1200 ºC. The batch is left at this temperature for 2 h to complete homogenization of the melt. After this time, the furnace was programmed to cool down at a speed of 10 ºCmin^{-1} until it reaches 900 ºC (called intermediate temperature) and then, the crucible is quenched to room temperature. Depending on the amount of rare earth and also of its nature, the intermediate temperature may change. The control of the crystal size is based on both cooling rate and intermediate temperature. Slower is the cooling rate bigger are the crystals. Bigger crystals can also be obtained by decreasing the intermediate temperature while maintaining the same cooling rate. However, large changes in these parameters lead to polycrystalline materials.

Isolation of the crystals: Crystals can be isolated from the parent glasses by chemical etching. Pieces of glass containing the crystals were placed in concentrated HNO_3 or HCl solutions and left for 12 h for the complete dissolution of the glass phase. The process can be accelerated by increasing the temperature of the acid solution, however, some of the crystals can also be attacked by at higher temperatures. From our experiments, Nd-$Y_3Al_5O_{12}$ were the only garnet to be attacked by the concentrated acid solutions, even at room temperature. In this case, to obtain the crystals, a diluted HCl solution was used to dissolve the parent glass. Thus, the time to isolate the crystals increased to 24 h. After dissolution of the glass phase, the crystals were whashed with isopropanol alchool for three times before be placed into a oven heated at 100 ºC.

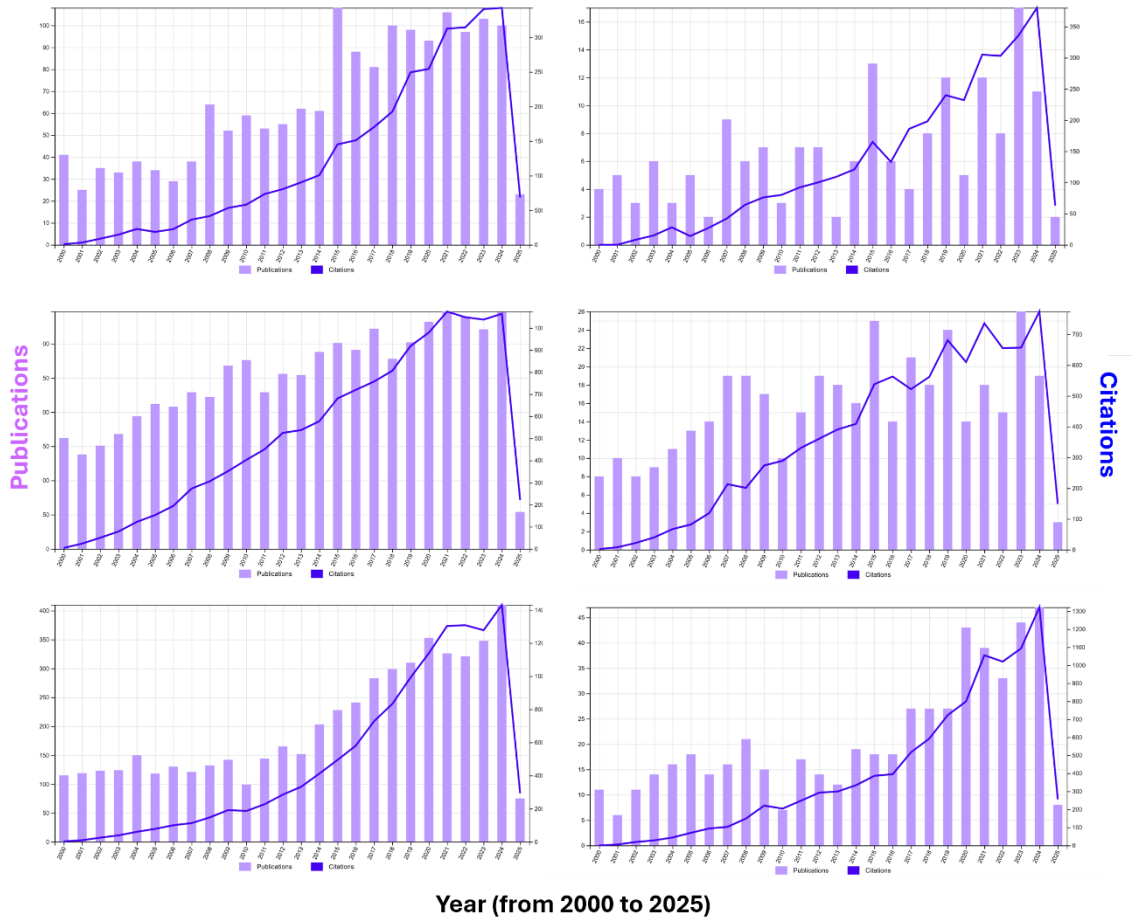

Figure S1 – Number of papers and citations for garnets and rare earths containing garnets (from upper to the bottom) Gallium, Aluminum, and Iron. These data were obtained from the Clarivate database using the words: Gallium garnets and rare earth gallium garnets; aluminum garnets and rare earth aluminum garnets; iron garnets and rare earth iron garnets.

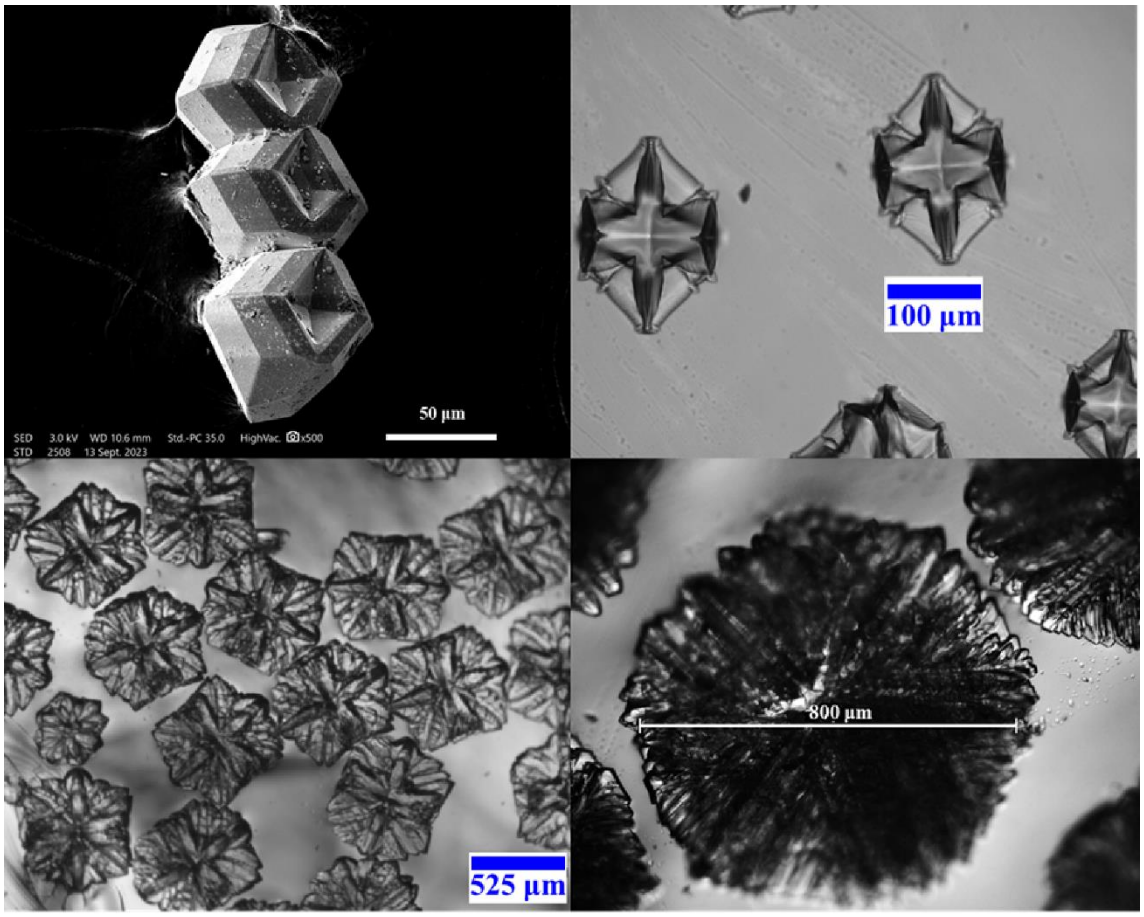

Figure S2 – Different morphologies during attempting to obtain bigger crystals

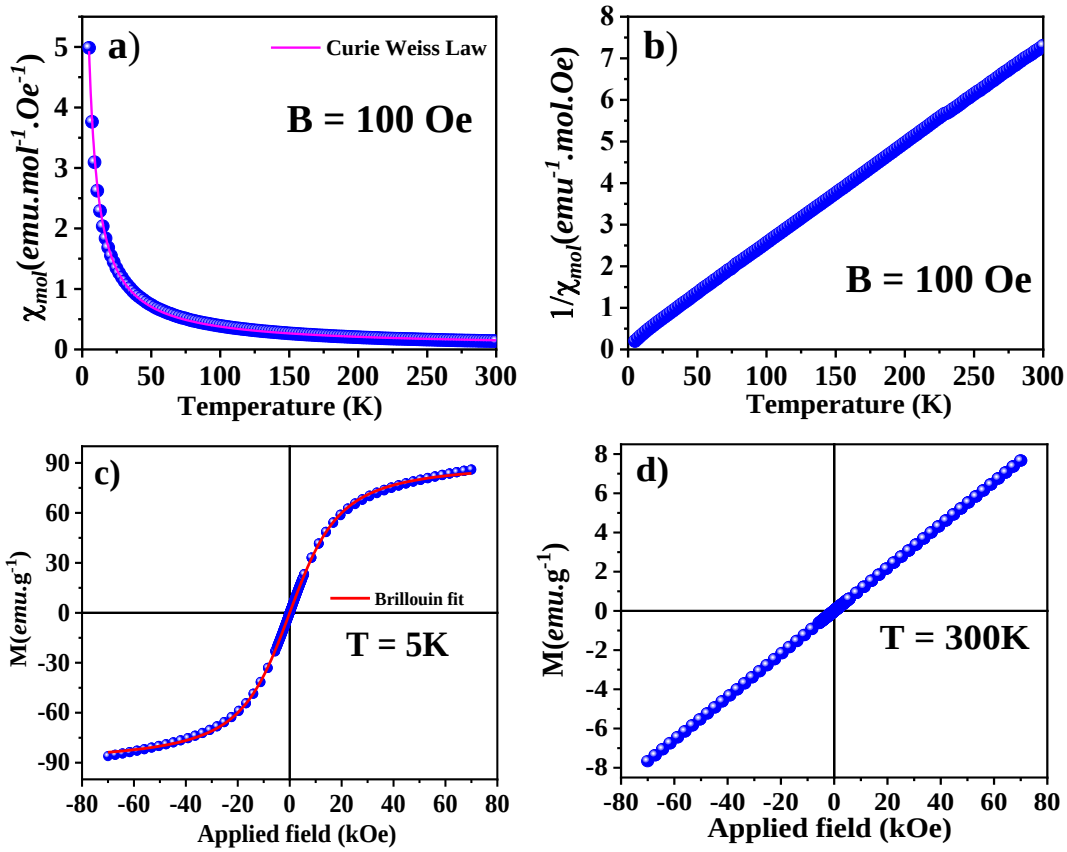

Figure S3 - Magnetic studies for TGG single microcrystal extracted from the glass. **(a)** Temperature dependence (ZFC) of the magnetic susceptibility ($\chi_M \times T$) at 100 Oe, with the solid pink line represent the fit to the Curie-Weiss law. **(b)** Temperature dependence of the inverse of the magnetic susceptibility ($1/\chi_M$). Magnetization as a function of the applied magnetic field (M × H) is shown for TGG single crystals matrix at **(c)** 5 K and **(d)** 300 K, respectively, with the red line represent the Brillouin fit.

The isothermal magnetization hysteresis curve displays typical paramagnetic characteristics.